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Title: THEORY OF ORGANIC ANALYTICAL REAGENTS by I. M. Korenman (USSR)

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THEORY OF ORGANIC ANALYTICAL REAGENTS

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Not only dimethylglyoxime, but also other alpha-dioximes react with nickel $\sqrt{1}$, 2, $3\sqrt{2}$. Alpha-dioximes react with other ions besides nickel. Thus, dimethylglyoxime is capable of reacting with salts of ferrous iron, cobalt, palladium, platinum, and copper 27. Colored compounds are also yielded by salts of rhodium [h], iridium [5], rhenium [6], gold [7] and bismuth [8]. Other alpha-dioximos exhibit activity within approximately the same range. For instance, alpha-benzildioxime forms colored, difficultly soluble compounds with salts of nickel, ferrous iron, palladium [9], platinum, silver [10], copper [11], and bismuth [12]. Methylglyoxime reacts with salts of nickel, palladium, silver, copper, and ferrous iron 137, while alpha-furildioxime yields precipitates with salts of nickel, palladium, rhodium, platinum, and ruthenium $\sqrt{11}$. Generally speaking, Fe++, Co, Ni, Pd, and Cu ions react with all alpha-dioximes. Ru, Rh, Pd, Ir, Re, Bi, Au, and Ag ions react with only some of them. Fe++ gives with the reagents in question a reaction which is highly specified and more sensitive than that ymelded by the nickel cation; substances reacting in this manner may be described as specific reagents for Fe++ or some other ion with greater justification than naming them reagents for nickel.

A number of organic substances which does not contain the alpha-dioxime grouping still reacts with nickel ions and cations of other elements lying within the range indicated above $\sqrt{15}$, 16, 17, 18, 19, 20, 21, 227. The fivering inner complex shown below is common to the products formed by the compounds involved, which possess the groupings indicated in the formulae.

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Irrespectively of the position of the double bonds, the following formation of a cyclic complex salt takes place in all of the four cases thus formulated:

$$\begin{array}{cccc}
C & C & C & C & C \\
 & & & & & & \\
N & & & & \\
N & & & & &$$

Depending on the position of double bonds and the nature and position of the radicals combined with the basic functional group which is common to all of the reagents discussed hitherto, we have subgroups of reagents and individual reagents exhibiting specific properties as far as their application in analysis is concerned.

It has already been noted that nickel in the five membered ring may be replaced by other ions. The atoms of carbon and nitrogen may also be replaced by other atoms without affecting the general range of reactive ability of the compound 21, 25, 26, 27. In regard to analogous compounds of this class, investigations carried out in our laboratory by S. A. Orlova have shown that crystals of nickel and palladium nitrosoguanidine are very similar in shape to the corresponding compounds of the cations in question with dimethylglyoxime.

A number of monooximes of dioxocompounds exhibits a reactivity similar to that of the substances mentioned above and forms five-ring complex salts in which the complex-forming atom of nitrogen is replaced by oxygen 21, 25, 26. N'-hydroxy-N-(3-nitrophenyl)-N'-benzamidine 27 gives an orange-yellow precipitate with nickel salts, forming the complex

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The same compound forms red-brown salts of cobalt and copper as well as a blue-violet iron salt, i.e., has a range of reactivity which approaches that of dimethylglyoxime and other reagents of this group which are enumerated above. N'-hydroxy-N-phenyl-N'-benzyl-formamidine behaves similarly.

2,2'-dipyridyl is closely related to the reagents described above as far as its mode of action is concerned 287. With ferrous iron, it forms the complex shown below:



The main valencies of the Fe⁺⁺ ion do not participate in the formation of this complex. Dipyridyl also forms the red salt $\angle (C_{10}H_8N_2)_3N_2/Br_2$, a corresponding yellow cobalt salt, the insoluble red cuprous salt $\angle (C_{10}H_8N_2)$ $C_{10}M_3$, and other compounds of this type $\angle 297$.

One may mention in this connection metal-cthylene diamine complex salts of the type

$$\begin{bmatrix} & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\$$

The nickel tri-(ethylene diamine) cation which corresponds to this formula is used as a reagent for the $S_2O_3^{\pi}$ ion; the thiosulfate precipitates in the form of violet crystals $\angle 307$. Nickel tri-(ethylene diamine) diiodide has a red-violet color and is soluble in water with difficulty. Derivatives of ethylene diamine also form colored, difficultly soluble complex salts of nickel, cobalt, cupric copper, platinum, etc $\angle 317$. Furthermore, ethylene diamine and its derivatives form with salts of a number of metals complex salts of the type yielded by 2,2'-dipyridyl, although the specific five-ring grouping is different here. The substitution of an atom of nitrogen with carbon in the specific group is also possible in this class of reagents.

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Thus, 2-pyridylhydrazine exhibits reactions of limited sensitivity towards Fe^{++} and Co^{++} (32, 337).

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- 4 -

CONFIDENTIAL

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